

Structural Changes in Ferronematic Liquid Crystals Studied by Surface Acoustic Waves

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Abstract

The response in attenuation of surface acoustic wave (SAW) of frequency 30 MHz propagating along ferronematic liquid crystals (6CHBT) to both electric and low magnetic field (up to 0.25 T) has been studied experimentally. Two low volume concentrations ($\Phi_1=1\times 10^{-5}$ and $\Phi_2=1\times 10^{-4}$) of spherical magnetic nanoparticles were added to liquid crystal during its isotropic phase. In contrast to undoped 6CHTB the distinctive SAW attenuation responses induced by both electric and magnetic fields in ferronematic liquid crystals below Fréedericksz transition have been observed suggesting structural changes and the orientational coupling between the magnetic moment of magnetic particles and the director of the liquid crystal. The geometrical re-ranking of magnetic nanoparticles was registered for some orientations of magnetic field, too. Observed results confirmed the significant influence of the presence of magnetic nanoparticles on the structural properties of 6CHTB.

Keywords: Ferronematics; Liquid crystals; Magnetic particles; Structural changes; Surface acoustic wave

1 Introduction

Liquid crystals (LC) have attracted a lot of attention due to the unique electro-optical and thermo-optical properties and have been used in numerous applications. Recently, LC suspensions containing nanocolloidal particles have registered additional great attention for many practical applications such as nanosensors, liquid crystal display industry, optical processing, biosensors, photonics and magneto-optics. The new applications are in need of new materials with exotic properties and new technologies. For example, LC materials for telecommunications usually require LCs with strong birefringence but low refractive index, adaptive LC optics needs LC materials with huge birefringence and low viscosity (Quan, 2012). Ferroelectric particles have the strong effect on the optical and dielectric properties of the nematic matrix. The increase of birefringence and dielectric anisotropy of the nematic matrix by

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the particles is caused by a giant dipole moment of ferroparticles that change the intermolecular interaction in the LC matrix and gives a direct contribution to the value of the effective dielectric constants of the matrix. Introduction of the particles leads to the decrease of driving voltages, increase of the reflection contrast and the steepness of the transition (Li, et al., 2006). Stable colloidal suspensions of monodomain ferromagnetic particles in nematic LC called ferronematics, attract noticeable interest because their response to an external magnetic field oversteps substantially that of pure nematics. The most essential feature of these systems is a strong orientational coupling between the magnetic particles and the liquid crystal matrix. The applied magnetic field changes the orientation of the magnetic particles and due to the coupling between magnetic particles and liquid crystal molecules the director follows it.

Experimental studies showed that the behaviour of liquid crystals (LCs) can be changed under the influence of electric and magnetic fields. LCs can be orientated under magnetic or electric fields due to their anisotropic properties. However, because of the small value of the anisotropy of the diamagnetic susceptibility, the magnetic fields necessary to align liquid crystals have to reach rather large values ($B > 1$ T). In an effort to enhance the magnetic susceptibility of liquid crystals, the idea of doping them with fine magnetic particles was introduced, firstly theoretically (Brochard & de Gennes, 1970). The authors predicted that a rigid anchoring $\mathbf{m} \parallel \mathbf{n}$, where the unit vector \mathbf{n} (director) denotes the preferential direction of the nematic molecules and the unit vector \mathbf{m} denotes orientation of the magnetic moment of the magnetic particles, would result in ferromagnetic behavior of the nematic matrix. The experiments confirmed the existence of considerable orientational and concentrational effects in liquid crystals doped with magnetic particles as well as the fact that the essential feature of these systems is a strong orientational coupling between the magnetic particles and the liquid crystal matrix (Liebert & Martinet, 1979), (Figueiredo, Liebert, & Levelut, 1984), (Burylov, 1995).

Acoustic (ultrasonic) methods were mostly used for the characterization of LC elastic and viscous parameters especially in the vicinity of phase transitions, more frequently in nematic liquid crystals (NLCs) (Pasechnik, Chigrinov, & Shmeliova, 2009). In particular, the surface acoustic wave (SAW) was used to determine the viscosity distribution in LC layer depending on applied electric field and to study the effect of structural transformation in LCs under the effect of acoustic oscillations (Kapustina, 2008), (Sato & Ueda, 1981), (Moritake, et al. 2011). The SAW can be also utilized for LC realignment based on the acousto-optic effect, as the SAW-driven LC light shutter was developed by integrating a cured LC film and a pair of interdigital transducers onto a piezoelectric substrate (Liu, et al., 2011) or SAW sensor (Tomašovičová, et al., 2014). In this contribution we present the utilization of SAW to study the structure changes in LCs doped with magnetic particles induced by electric and low magnetic fields and corresponding orientational coupling between the magnetic particles and the liquid crystal matrix.

2 Experimental method

The ferronematic samples studied were based on the thermotropic nematic 6CHBT 4-(trans-4-*n*-hexyl-cyclohexyl)-isothiocyanato-benzene. 6CHBT is an enantiotropic liquid crystal with a low melting point and high chemical stability (Patrash & Zellers, 1994). The temperature of the nematic–isotropic transition (clearing point) of the nematic studied is $T_{N-I} = 42.8$ °C. The nematic samples were doped with a magnetic suspension consisting of Fe_3O_4 particles (diameter $d \sim 10$ nm, standard deviation $\sigma = 0.28$) coated with oleic acid as a surfactant. The size and morphology of the particles were determined by transmission electron microscopy (TEM). The doping was simply done by adding this suspension, under continuous stirring, to the liquid crystal in the isotropic phase. Due to the small volume concentrations of the magnetic particles ($\Phi = 10^{-5}$ – 10^{-4}) and surfactant in the prepared ferronematic samples, interparticle dipole–dipole interactions are avoided. The homogeneity and

stability of the samples were verified by optical microscopy and by dielectric measurements, indirectly (Tomašovičová, et al., 2008).

The surface acoustic waves of fundamental frequencies 10 and 20 MHz were generated using an interdigital transducer (IDT) evaporated on the LiNbO_3 delay line by the Pulse Modulator and Receiver - MATEC 7700 and other transducer was used for receiving the surface wave. The acoustic attenuation was measured using Matec Attenuation Recorder 2470 A. However, further harmonic frequencies 30, 40 and 50 MHz could be used, too. The frequency 30 MHz, after many carried out experiments, appeared the most sensitive SAW frequency for structural changes study. The samples of LCs were placed on the top of the LiNbO_3 . Figure 1 shows the experimental arrangement, the LC layer was located on the center of the acoustic delay line and sandwiched between delay line and glass plate, both coated with gold evaporated electrodes. The LC cell thickness ensured by used spacer was $D \approx 100$ nm.

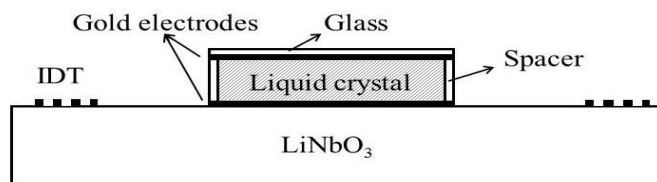


Figure 1: Schematic arrangement of LC cell on LiNbO_3 delay line for SAW investigation.

3 Results and discussion

Structural changes in LCs were monitored using the attenuation measurements of SAW propagating along the interface between the LiNbO_3 delay line and LC cell. In initial arrangement, the LC had a planar alignment when the director \mathbf{n} was parallel to the electrodes and electric field was applied perpendicular to them (Figure 2). The electric field turned the director to its direction so that LC molecules changed orientation to perpendicular to the surface of electrodes and SAW attenuation increased. The magnetic field could be applied both parallel and perpendicular to electrodes and this way to stabilize the initial orientation of magnetic particles as well as LC molecules or to highlight the turning effect of electric field. However, from the viscosity distribution measurement (Tomašovičová, et al., 2008) follows that the reorientation of molecules depends on the electric field intensity and

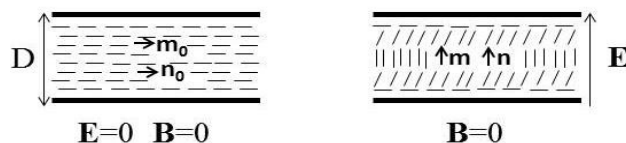


Figure 2: Cross section of the LC cell in the initial state (a) and after electric field application (b).

molecules change the orientation gradually and start at center. Figure 3 shows the effect of applied voltage on SAW attenuation of 6CHBT doped with Fe_3O_4 ($\Phi=10^{-4}$) for the alternating switch on and

off after two minutes. We can see the dynamic of this switching effect, LC molecules change the orientation under electric field in a few seconds. However, the magnitude of this effect depends on the intensity of applied electric field. The dependence of SAW attenuation changes on applied electric field for LC 6CHBT consisting of Fe_3O_4 particles ($\Phi = 10^{-4}$) for zero magnetic field as well as for magnetic field $B = 250$ mT are illustrated in Figure 4. It can be seen that for the voltage higher than 5 V strong changes of acoustic attenuation are registered that indicates the massive reorientation of LC

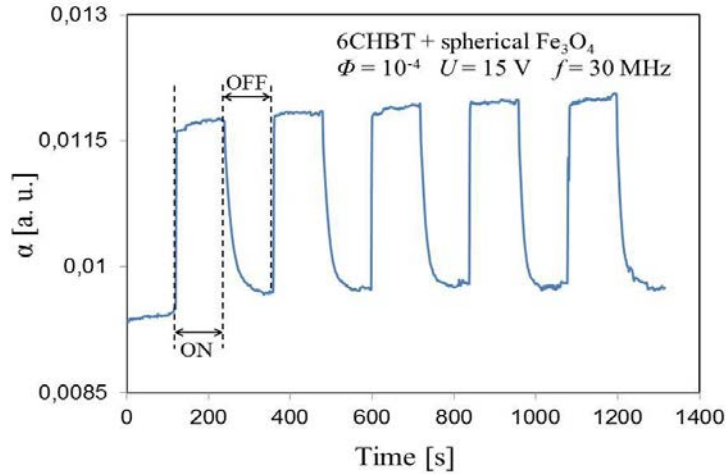


Figure 3: Effect of applied voltage (15V) on SAW attenuation for 6CHBT doped with Fe_3O_4 ($\Phi = 10^{-4}$).

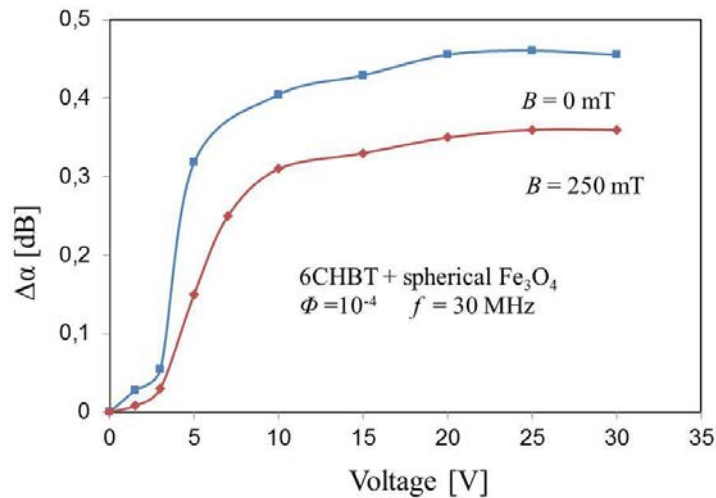


Figure 4: Dependence of SAW attenuation changes on applied electric field measured at zero magnetic field and at magnetic field $B = 250$ mT ($B//E$).

molecules. In the case of zero electric field the LC molecules can be reoriented also by magnetic field perpendicular to electrode surfaces, although with much less effect. When the electric field is applied at the constant magnetic field, the changes of acoustic attenuation are strong but because of the partial effect of magnetic field, not such strong as in the case of zero magnetic field. The saturation of achieved changes of SAW attenuation for voltages higher than 25 V represents the situation when the most of LC molecules should be reoriented. In pure 6CHBT liquid crystal the effect of applied electric field on acoustic attenuation changes were not so strong. All these experimental observations

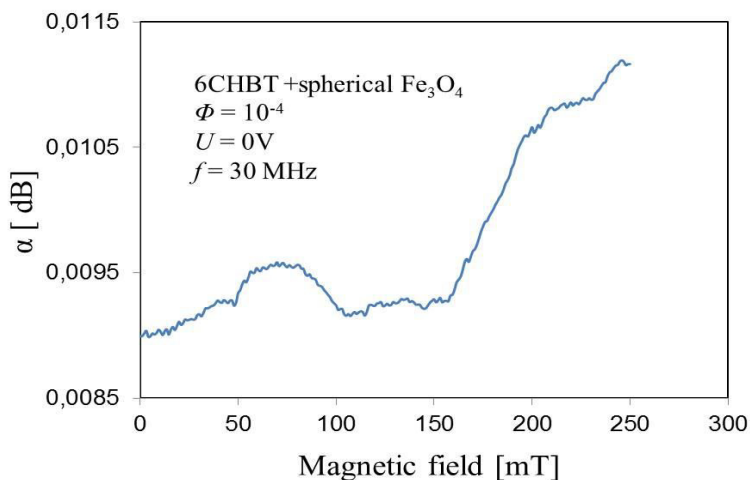


Figure 5: Dependence of SAW attenuation on magnetic field for 6 CHBT doped with Fe_3O_4 .

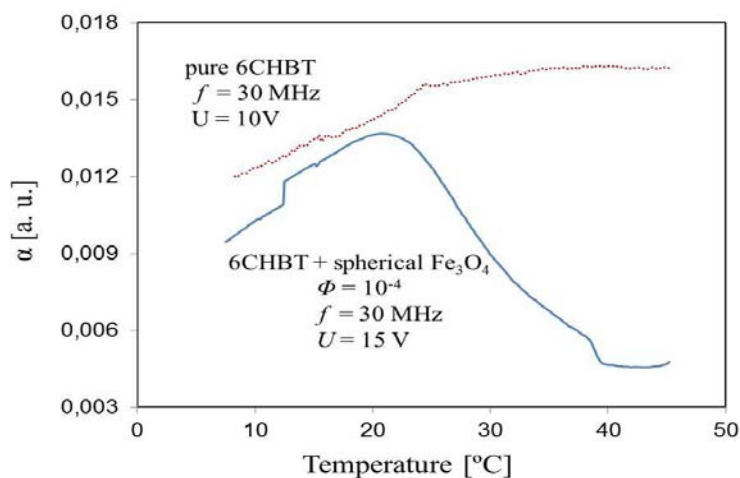


Figure 6: Temperature dependence of SAW attenuation for pure 6 CHBT and doped with Fe_3O_4 .

definitely confirm the role of magnetic particles in LC and their interaction with liquid crystal molecules and coincide with previous results obtained investigating the dielectric behavior of the same LCs (Tomašovičová, et al., 2008), (Tomašovičová, et al., 2013), (Kopčanský, et al., 2010), (Kopčanský, et al., 2013).

The dependence of SAW attenuation on magnetic field, measured up to 250 mT, shows that the process of reorientation of magnetic particles and due to their coupling also LC molecules is probably connected also with some structure changes of particles. It can be supposed that some aggregation of particles to some structures as dimers or trimers could occur.

Figure 5 illustrates the dependence of acoustic attenuation for LC 6CHBT doped with Fe_3O_4 particles ($\Phi = 10^{-4}$) at zero electric field. The observed behavior indicates that some process of aggregation except the process of reorientation of magnetic particles can occur, too. The temperature dependence of acoustic attenuation was measured for both pure LC and LC consisting of Fe_3O_4 particles (Figure 6). While the temperature dependence of pure 6CHBT shows only slow increase indicating the role of thermal motion on the interaction of surface acoustic wave and LC molecules and no structural transition is registered the temperature dependence in the case of doped 6CHBT shows after the initial increase to temperature of 21-22 °C also the decrease and both melting and clearing points are registered, too. The reason of the observed decrease could be in the process of structural changes of magnetic particles due to the increasing temperature. The registration of both transition points is probably the result of coupling between magnetic particles and LC molecules that sharpen the changes realized during the transition point.

Similar results were observed on 6CHBT doped with lower concentration of magnetic particles ($\Phi = 10^{-4}$), however, with weaker effects of both electric and magnetic fields.

4 Conclusions

In this contribution we presented the utilization of SAW to study the structure changes in 6CHBT doped with magnetic particles Fe_3O_4 induced by electric and low magnetic fields that confirmed previously supposed orientational coupling between the magnetic particles and the liquid crystal matrix. Various experimental measurements were done including the investigation of the effect of electrical and magnetic fields both separately and together as well as temperature and time influence. All obtained results validated the role of orientational coupling between the magnetic moment of magnetic particles and the director of the nematic liquid crystal and the possibility to better control of LC molecules using the combination of electric and magnetic field. However, further study in combination with optical methods should obtain new interesting results and also eliminate own role of SAW on the reorientation of LCs.

Acknowledgement

This work was supported by VEGA project 2/0045/13 and by project ITMS: 26210120021, co-funded from EU sources and European Regional Development Fund. Authors also would like to thank to Mr. František Černobila for technical assistance.



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